The Bond Energy and the Composition of Metal Oxides

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ABSTRACT

The relation between the bond energy of metal oxides and their composition has been discussed. To compare the bond energy of oxides of various compositions the cohesive enthalpy per one mole of oxygen atoms was used. The value of this enthalpy was calculated from thermochemical data. A linear relation between the cohesive energy and the composition was found for oxide phases of the same metal. The reasons for the lack of stability of oxides of type MO and M_2O_3 where M is Mo, W, Re, Ru, Os etc. have been indicated. The criteria for the formation of the above oxides have been given. Furthermore, minimum cohesive enthalpies needed to obtain thermodynamically stable phases have been calculated. The dependence of cohesive enthalpy on melting temperature and melting heat has been discussed.

Keywords: Metal oxides; Bond energy; Cohesive energy

1. INTRODUCTION

The bond energy of compounds is crucial for their properties. It can be obtained basing on experimental thermodynamic data (thermodynamic cycle) or theoretically /1-7/. The bond energy for ionic crystals can be obtained in a relatively easy way /1,2/. There is also a number of semi-empirical methods, which allow to evaluate the bond energy for covalently-bound crystals /3/. A good agreement between theoretically calculated and experimental values was obtained for ionic crystals (alkali metals chlorides etc.) or typical covalent ones (BN, GaAs, CdTe, InSb, ZnS, CdS etc.), whereas in the case of other chemicals, oxides included, the differences observed are quite significant /4/. As well as the values of the cohesive enthalpy calculated on the basis of thermodynamic properties, also the enthalpy of formation of a given oxide is often used in the analysis of the interactions. These values depend by definition not only on the bond energy, but also on the sublimation heat of the metal and the dissociation energy of the oxidant. This problem was widely discussed in an earlier work /8/. In chemical tables /9/ one can find lattice energy for a given compound, calculated for ionic structures. This approach in many cases, where a polarized bond is present, or more generally, where there is a covalent contribution to the interaction, does not yield the actual bond energy.

The development of quantum methods in recent years and the calculating capabilities of fast computers made possible the evaluation of the bond energies for relatively big crystal clusters /7/. These values allow the demonstration of the changes in the interactions, e.g. as a result of point defects or doping. However, there is no data that could possibly be used for the purpose of comparison of different oxides, especially if atoms/ions of metal have very different electronic structures (ions of s, p, d metals)

In the present work the oxide phases of metals were examined, dependent on their cohesive energy (energy of atomization) and on their composition in order to determine correlations, especially in the case of various oxide phases of the same metal.

2. COHESIVE ENERGY (ENERGY OF ATOMIZATION)

In order to analyze the changes in the interactions in oxides with different compositions and crystal structures we decided to use the enthalpy of atomization. In the case of crystals this value is frequently called the cohesive energy. The above energy is defined in thermodynamics as the heat effect of the following reactions (at 0 K):

$$\begin{aligned} & M_aO_b = aM_{(g)} + bO_{(g)} \\ & E_{\mathrm{coh}\,M_aO_b} \cong \Delta H^0_{\mathrm{coh}\,M_aO_b} = \\ & -\Delta_f H^0_{M_aO_b} + a\,\Delta H^0_{\mathrm{sub}\,M} + b/2\,\Delta H^0_{\mathrm{dis}O_2} \end{aligned} \qquad (1)$$

where $E_{\mathrm{coh}\,M_aO_b}$ denotes molar cohesive energy of M_aO_b oxide. Basing on thermodynamic cycle /8/, it is easy to show that the cohesive enthalpy is the sum of enthalpy of formation of the oxide ($-\Delta_f H^0_{M_aO_b}$), enthalpy of metal sublimation ($\Delta H^0_{\mathrm{sub}\,M}$) and enthalpy of oxygen dissociation ($\Delta H^o_{dis\,O_2}$). Therefore, to calculate the cohesive energy (according to Eq. (1)) the enthalpies of formation of oxides were used:

$$a\,M + b/2\,O_2 = M_aO_b \quad \Delta H^0_{M_aO_b} \qquad (2)$$

as well as the enthalpies of metal sublimation and enthalpy of oxygen dissociation. The cohesive energy per one mole of oxide is the total energy of interactions (bonds) between a certain number of metal atoms (a) and oxide atoms (b). In order to compare the cohesive energies of the oxides of various compositions the value of the cohesive energy per one mole of oxygen atoms should be used as a convenient parameter.

$$\begin{aligned} & 1/b\,M_aO_b = M_{a/b}O = a/b\,M_{(g)} + O_{(g)} \\ & E_{\mathrm{coh}} = E_{\mathrm{coh}\,M_{a/b}O} = 1/bE_{\mathrm{coh}\,M_aO_b} = \\ & 1/b\Delta H^0_{\mathrm{coh}\,M_aO_b} \cong \Delta H^o_{\mathrm{coh}} \end{aligned} \qquad (3)$$

The amount of this energy is connected with a definite structural element which contains one mole of oxygen atoms and the corresponding number of metal atoms (a/b) resulting from the stoichiometric formula of the $M_{a/b}O$ oxide. It is a result of the interaction not only with nearest atoms, but also with atoms that are located in more distant spheres of interaction. It should be noted that the above value is a total bond energy in oxides with different amount of metal relative to oxygen (M/O), in which metal ions have different oxidation states or mixed valence can occur. The above parameter (E_{coh}), will be called further the *effective molar cohesive energy* (bond energy) per one mole of oxygen atoms. Because the bond energy defined in this way does not differ much from the standard cohesive enthalpy, the $\Delta H^o_{\mathrm{coh}}$ values will be used (at 298 K) in the present study.

3. COHESIVE ENTHALPIES OF THE OXIDES OF THE SAME METAL

The parameter introduced earlier, the effective cohesive enthalpy, $\Delta H^o_{\mathrm{coh}}$, makes it possible to compare the oxides of different compositions, especially the oxides formed by the same metal. In **Fig.1** the relation between the effective cohesive enthalpy $\Delta H^o_{\mathrm{coh}}$ of the $M_{a/b}O$ oxides and their composition a/b (M/O ratio) is shown. The cohesive enthalpy was calculated using Eq. (1) and (3) and available thermodynamic data /10-13/. In the case of TiO, VO, NbO having non-stoichiometric composition, their real composition was used, e.g. the composition of the oxide being in the equilibrium with metal ($M/M_{1-y}O_{1-x}$). As it can be seen, the resulting linear correlation is very good. **Table 1** contains parameters of linear equations of type:

$$\Delta H^o_{\mathrm{coh}} = \mathrm{A}\,a/b + \mathrm{B} \qquad (4)$$

along with correlation coefficients R^2. Comparing the respective straight lines for the oxide phases of different metals one can assume that the lines for transition metals from groups 4-6 have similar slopes. The oxides of Mn, Fe and Co have slightly smaller slope. The points for the remaining oxides of metals from groups 12-15 are located on lines that have slopes two times lower than the previous ones. The oxides of the f-electron metals with the composition a/b < 0,666 (Fig.1b) have similar or higher (Tb and U oxides) slopes relatively to those for transition metals. However, for the MO and M_2O_3 oxides of Eu and Pu the slopes are similar to those of the oxides of the metals from main groups (Table 1).

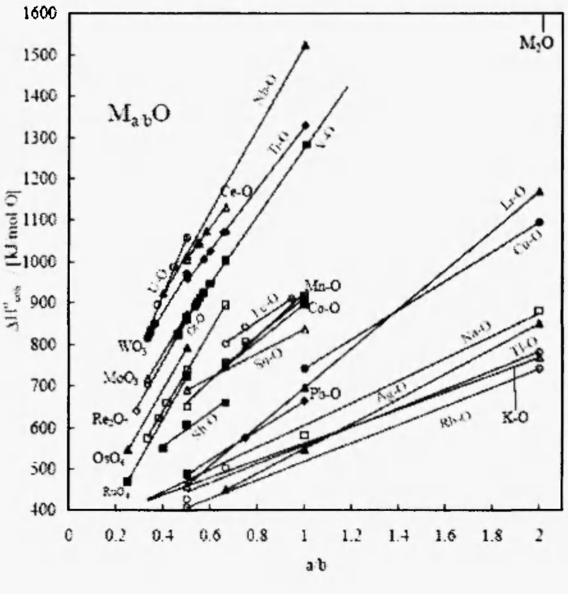

Fig. 1a

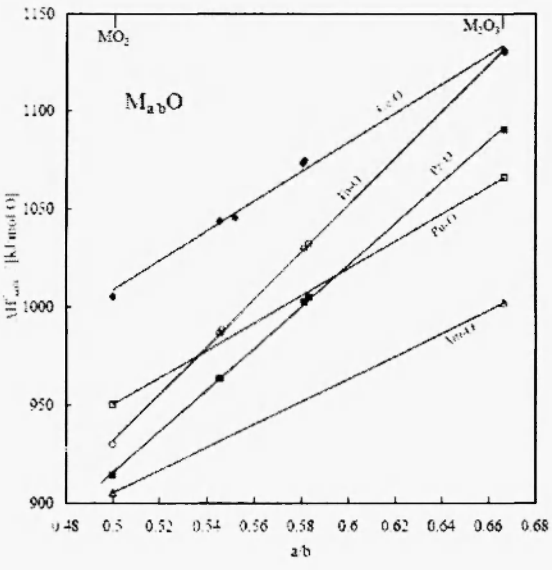

Fig. 1b

Fig. 1: The dependence of the effective cohesive enthalpy (ΔH^o_{coh}) of $M_{a/b}O$ oxides on the a/b ratio (a) and the same dependence for the oxides of f-electron metals (b).

Table 1

Parameters for the dependence of the effective cohesive enthalpy (ΔH^o_{coh}) of $M_{a/b}O$ oxides of the same metal on the a/b ratio ($\Delta H^o_{coh} = Aa/b + B$) [kJ/mol O]. R^2 is the correlation coefficient.

oxides	A	B	R^2	Ph.N.
Li_2O-Li_2O_2	472.38	224.50	1	2
Na_2O-NaO_2	268.63	337.07	0.9892	3
K_2O-K_2O_2	206.03	355.94	1	2
K_2O-KO_2	194.57	396.04	0.9144	3
Rb_2O-RbO_2	223.30	294.94	1	2
TiO-TiO_2	748.08	579.25	0.9991	6
VO-V_2O_5	833.83	444.74	0.9986	13
NbO-Nb_2O_5	1008.00	515.51	0.9998	3
Cr_2O_3-CrO_3	956.18	259.12	0.9997	6
MoO_2-MoO_3	936.25	405.59	1	2
WO_2-WO_3	930.29	505.52	0.9995	5
MnO-MnO_2	526.81	398.24	0.9873	4
ReO_2-Re_2O_7	966.32	376.81	0.999	3
FeO-Fe_2O_3	378.74	552.22	0.9943	3
RuO_2-RuO_4	1014.20	216.39	1	2
OsO_2-OsO_4	987.39	298.67	1	2
CoO-Co_3O_4	457.95	454.45	1	2
RhO-Rh_2O_3	447.57	449.89	1	2
Cu_2O-CuO	352.53	390.02	1	2
Ag_2O-Ag_2O_3	300.85	248.23	0.9999	3
Tl_2O-Tl_2O_4	225.72	331.40	0.9899	3
SnO-SnO_2	292.53	544.38	1	2
PbO-PbO_2	356.42	308.06	1	2
Sb_2O_3-Sb_2O_5	409.34	391.99	0.9706	3
Ce_2O_3-CeO_2	751.00	633.28	0.9927	7
Pr_2O_3-PrO_2	1057.90	386.47	0.9994	6
EuO-Eu_2O_3	306.47	716.59	1	2
Tb_2O_3-TbO_2	1199.30	332.27	0.9997	5
UO_2-UO_3	1417.30	353.56	0.9903	4
Pu_2O_3-PuO_2	692.71	603.96	1	2
PuO-Pu_2O_3	282.61	877.36	1	2
Am_2O_3-AmO_2	584.20	612.86	1	2

* - Ph.N – phase number;

The comparison of the data given in Fig.1 implies that many oxide phases of the same metal are formed by d- and f-electron elements (Ce, Pr, Tb) and main groups metals of the 5th period (Tl, Pb and (Bi)). This fact is usually attributed to the possibility of different stable oxidation states for ions of these metals and, in the case of the d-electron metals, by the presence of d-orbitals or dsp-hybrid orbitals in the bond. The decrease of the cohesive enthalpy with the metal content may seem obvious, even if the decrease of M/O ratio causes the increase of the oxidation state and thus the strengthening of the electrostatic interaction. More striking could be the fact of obtaining practically linear change in the cohesive enthalpy with the concentration in such a wide range. It should be noted that the relations obtained are not only valid for the oxides with a given oxidation state of the ion (MO, M_2O_3, MO_2 etc.) but also for the oxide phases in with ions having different oxidation states and their ratios in different oxides changing (oxide phases of Ti, V, Cr, Ce, Pr, U etc.). Therefore, even if in the oxide structure we have ions in various oxidation states and with different strength of the electrostatic interaction, the total energy of the interaction with the same number of oxide atoms changes linearly.

4. FORMATION CRITERIA OF THE MO AND M_2O_3 OXIDES OF HIGH-MELTING METALS

As seen from Fig.1, many metals from groups 4-10 do not form oxides of type MO and M_2O_3 while they form MO_2 and higher oxides. If the MO, M_2O_3 or MO_2 oxide is in equilibrium with metal, one can describe this state by the following equations:

$$M + 1/2O_2 = MO \quad \Delta G^o_5 = \Delta_f G^o_{MO} \qquad (5)$$

or

$$2/3M + 1/2O_2 = 1/3M_2O_3 \quad \Delta G^o_6 = 1/3\Delta_f G^o_{M_2O_3} \qquad (6)$$

or

$$1/2M + 1/2\,O_2 = 1/2MO_2 \quad \Delta G^o_7 = 1/2\Delta_f G^o_{MO_2} \qquad (7)$$

According to thermodynamics, for the M_2O_3 or MO oxide to be stable, its standard Gibbs energy of formation must be lower than $\Delta_f G^o_{MO_2}$ or $\Delta_f G^o_{M_2O_3}$ and, more precisely, the following condition must be satisfied:

$$\Delta_f G^o_{MO} < 1/3\Delta_f G^o_{M_2O_3} < 1/2\Delta_f G^o_{MO_2} \qquad (8)$$

In analogy to Eqs.(1) and (2) the standard cohesive Gibbs energy is the sum of the standard Gibbs energy of formation of the oxide ($\Delta_f G^o_{M_aO_b}$), of metal sublimation (ΔG^o_{subM}) and of oxygen dissociation ($\Delta G^o_{dis\,O_2}$):

$$\Delta G^o_{coh} = -1/b\Delta_f G^o_{M_aO_b} + a/b\Delta G^o_{sub\,M} + 1/2\Delta G^o_{dis\,O_2} \qquad (9)$$

Combining condition (8) with Eq.(9) and using known values of $\Delta_f G^o_{MO_2}$ (or $\Delta_f G^o_{M_2O_3}$) for thermodynamically stable oxides and standard Gibbs energies of the sublimation of metal and the dissociation of the oxygen in a given temperature, one can calculate the minimum standard cohesive Gibbs energy of the MO or M_2O_3 oxides. If these oxides had ΔG^o_{coh} higher than the minimum value, they would be thermodynamically stable. As in the present study the cohesive enthalpies of the oxides at 298 K are discussed, the calculated minimum values of the cohesive enthalpy $\Delta H^{o\,(min)}_{coh}$ for the MO or M_2O_3 oxides are given in **Table 2**. For values higher than these the oxides would be stable and could exist in the equilibrium with MO_2 or M_2O_3 oxide. Hence, the calculations were performed for $\Delta_f H^o_{MO} = 1/3\Delta_f H^o_{M_2O_3}$ condition in the case of thermodynamically stable M_2O_3 oxides and $1/3\Delta_f H^o_{M_2O_3} = 1/2\Delta_f H^o_{MO_2}$ or $\Delta_f H^o_{MO} = 1/2\Delta_f H^o_{MO_2}$ condition in the case of stable MO_2 oxides (in the calculation the entropic part of ΔG^o_{coh} function was neglected). As can be seen from Table 2, the cohesive enthalpies of MO or M_2O_3 should be relatively high, e.g. for the ZrO and HfO oxides they should be much higher than the ΔH^{o}_{coh} for the TiO oxide. The values of $\Delta H^{o(calc)}_{coh}$ given in the 5th column of Table 2 were extrapolated using linear equations from Table 1 assuming that for these oxides the obtained dependence of ΔH^{o}_{coh} on a/b is valid. As can be seen, for individual oxides $\Delta H^{o(calc)}_{coh}$ are even higher than $\Delta H^{o(min)}_{coh}$. For the purpose of comparison, the values of the cohesive enthalpies of stable oxides, which were used to calculate minimum values of ΔH^{o}_{coh}, are given in the next column.

Table 2

The effective cohesive enthalpy of $M_{a/b}O$ oxides: minimum (ΔH^{o}_{coh}(min.)) and extrapolated from the linear equations (Table 1).

oxides	$\Delta_f H^o_{min}/b$ [kJ/mol O]	$\Delta H_{subM}/(a/b)$ [kJ/mol O]	ΔH_{coh}(min.) [kJ/mol O]	ΔH_{coh} (calc.) [kJ/mol O]	stable oxides	ΔH^o_{coh} [kJ/mol O]
ScO	636.7	378.1	1264.1		Sc_2O_3	1138.1
YO	635.5	421.6	1306.5		Y_2O_3	1165.9
ZrO	550.6	620.9	1420.9		ZrO_2	1110.4
Zr_2O_3	550.6	413.9	1213.9		ZrO_2	1110.4
HfO	559.2	619.6	1428.2		HfO_2	1118.4
Hf_2O_3	559.2	413.1	1221.6		HfO2	1118.4
Nb_2O_3	796.7	489.0	1136.7	1187.4	NbO_2	796.7
TaO	409.5	782.5	1441.3		Ta_2O_5	971.8
Ta_2O_3	409.5	521.7	1180.5		Ta_2O_5	971.8
TaO_2	409.5	391.3	1050.1		Ta_2O_5	971.8
CrO	380.4	397.7	1027.5	1215.3	Cr_2O_3	896.6
MoO	294.7	659.4	1203.4	1341.8	MoO_2	873.7
Mo_2O_3	294.7	439.6	983.6	1029.8	MoO_2	873.7
WO	295.0	851.6	1396.0	1435.8	WO_2	970.7
W_2O_3	295.0	567.7	1112.1	1125.7	WO_2	970.7
Re_2O_3	224.6	513.6	987.5	1021.0	ReO_2	860.0
ReO	224.6	770.4	1244.3	1343.1	ReO_2	860.0
RuO	152.6	643.1	1045.0	1230.6	RuO_2	723.5
Ru_2O_3	152.6	428.7	830.7	892.5	RuO_2	723.5
OsO	147.4	791.3	1188.0	1286.1	OsO_2	792.4
Os_2O_3	147.4	527.5	924.3	956.9	OsO_2	792.4
RhO	127.4	557.3	934.0		Rh_2O_3	748.3
RhO *	90.9	557.3		897.5		
IrO	120.2	665.7	1035.2		IrO_2	702.4
Ir_2O_3	120.2	443.8	813.3		IrO_2	702.4
SiO	454.8	107.7	1155.1		SiO_2	929.6
GeO	290.1	374.7	914.2		GeO_2	726.8
LaO	598.3	431.2	1278.9		La_2O_3	1135.1
CeO	599.1	422.9	1271.3	1384.3	Ce_2O_3	1130.4
PrO	603.6	355.9	1208.8	1444.4	Pr_2O_3	1133.9
NdO	603.0	327.8	1180.2		Nd_2O_3	1070.9

Table 2 (continued)

SmO	609.5	206.8	1065.7		Sm_2O_3	996.8
GdO	609.4	397.7	1256.5		Gd_2O_3	1123.9
TbO	622.2	389.0	1260.5	1531.6	Tb_2O_3	1130.8
DyO	621.5	290.6	1161.4		Dy_2O_3	1064.5
HoO	627.4	301.0	1177.8		Ho_2O_3	1077.4
ErO	633.0	317.4	1199.7		Er_2O_3	1093.9
TmO	630.0	232.4	1111.7		Tm_2O_3	1034.2
YbO	605.2	152.2	1006.8		Yb_2O_3	956.0
LuO	626.5	427.9	1303.7		Lu_2O_3	1161.1
ThO	613.6	597.6	1460.5		ThO_2	1161.7
Th_2O_3	613.6	398.4	1261.3		ThO_2	1161.7
UO	542.6	531.7	1323.7	1770.9	UO_2	1057.8
U_2O_3	542.6	354.5	1146.4	1298.4	UO_2	1062.2
NpO	514.6	465.2	1229.1		NpO_2	996.5
PuO	586.2	345.4	1180.9	1296.7	Pu_2O_3	1065.8
PuO *	565.2	345.4		1160.0		
AmO	563.5	67.9	1097.1		Am_2O_3	1002.3

* - experimental values

It is known that the binding forces of ions of transition metals, especially covalent contribution to the interaction energy, depend on the electronic configuration of ions (stable oxidation states), and consequently on the number of electrons on d orbitals and on the effective electrostatic interaction of the ion, which depends on nucleus charge and shielding ability of inner electron shells. In **Fig. 2** the relation between the effective cohesive enthalpy of transition metals oxides (group 3-7) and the number of electrons on d shell of respective ions is shown. The calculated minimum values of the effective cohesive enthalpy $\Delta H^{o(min)}_{coh}$ of M_2O_3 oxides of Mo, W, Re, Ru, Os, resulting from the condition (8) (Table 2) are also plotted in this figure. From Fig. 2 one finds that the cohesive enthalpies of the oxides of the same type which are in the same period decrease with the increase of the atomic number of metal. If the above character was conserved for M_2O_3 oxides of the metals discussed, the values of the cohesive enthalpy would be close to the enthalpies for M_2O_3 oxides of 3d metals, because the cohesive enthalpies for the Y_2O_3 and La_2O_3 oxides are only slightly higher than that of the Sc_2O_3. As the MO_2 oxides of 4d and 5d metals have higher cohesive enthalpies than analogous 3d oxides, also M^{3+} ions of those metals would interact stronger in the oxide structure. It should be expected that M^{2+} or M^{3+} ions will have lower binding ability than M^{4+} ions, but the increase of their content in the oxide in relation to MO_2 oxide should lead to the increase in the cohesive enthalpy. Simultaneously the repulsive contribution will increase. As a result, the cohesive enthalpy will not rise enough to fulfill the condition (8). It should be noted that the increase of the cohesive enthalpy should be big enough to balance the increase of the component of the sublimation of the metal $\Delta G^{o}_{sub\,M}$ (see Eq. 9) which is quite significant for high-melting metals.

In Table 2 for the RhO and PuO oxides the experimental data /12/ are given. These values are too low according to the present evaluation.

The above calculations and conclusions are of course valid for the temperature of 298 K, whereas for every higher value of the temperature the condition (8) should be satisfied. As stated before, the standard Gibbs energy of formation of the oxide ($\Delta_f G^{o}_{coh}$) depends not only on ΔG^{o}_{coh} but also on the enthalpy $\Delta G^{o}_{sub\,M}$ of metal sublimation and on the enthalpy $\Delta G^{o}_{dis O_2}$ of the oxygen dissociation (Eq. 9). These functions have different temperature relationships. In addition, in different oxides we have various amounts of metal (different a/b $\Delta G^{o}_{a/bM}$ component). Therefore, at a sufficiently high temperature, the condition (8) could be fulfilled and M_2O_3 or MO should be thermodynamically stable above the equilibrium pressure.

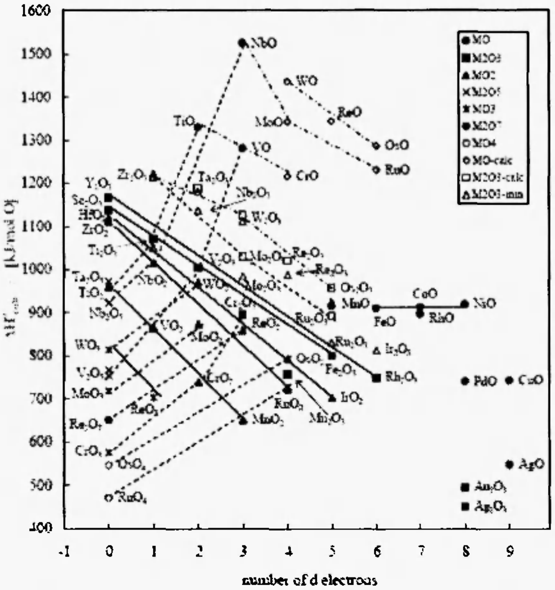

Fig. 2: The dependencies of the effective cohesive enthalpy (ΔH^{o}_{coh}) for the oxides of transition metals (groups 3-7) on the electronic configuration of ions d^{i}. The minimum values of the effective cohesive enthalpy $\Delta H^{o(min)}_{coh}$ calculated from the condition (8) are marked with ◊, the ΔH^{o}_{coh} values extrapolated from the equations in Table 1 are marked with Δ and □.

5. BOND ENERGY AND MELTING TEMPERATURE

The melting heat is a parameter that characterizes melting process. It should depend on the cohesive enthalpy. The relation between the melting enthalpy of the oxides $\Delta H^{m}_{M_{a/b}O}$ which is defined per one mole of oxygen ($1/b\,\Delta H^{m}_{M_aO_b} = \Delta H^{m}_{M_{a/b}O}$) and the effective cohesive enthalpy (ΔH^{o}_{coh}) is shown in **Fig. 3**. The values for the melting heat were taken from thermochemical tables /11,12/. As can be seen in Fig. 3, for a significant number of oxides there is a good linear correlation between the effective cohesive enthalpy and the melting enthalpy, while the points for the oxides of transition metals and these of metals from main groups are located on two separate straight lines. That should be attributed to the differences in the character of bonds. The above relations do not apply to the MnO, FeO, Fe_2O_3 oxides for which the obtained values of the melting enthalpy are too high. On the contrary SiO_2 has a very small value of the melting enthalpy, which is related to the covalent character of the bond.

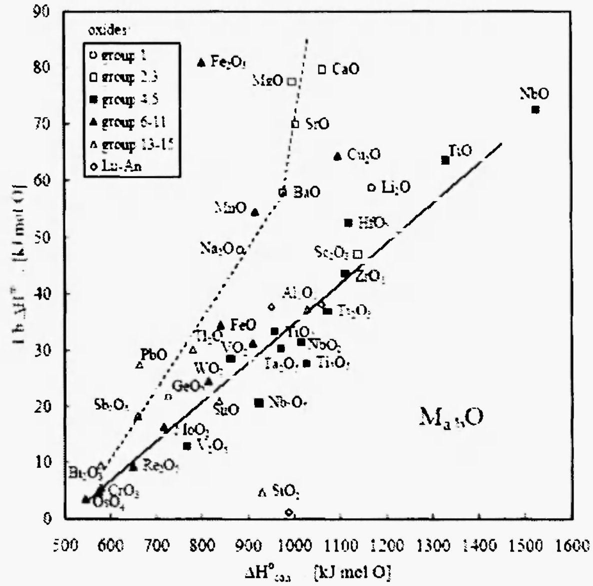

Fig. 3: The dependence of the melting enthalpy ΔH^{m} of the oxides per one mole of oxygen atoms on their effective cohesive enthalpy ΔH^{o}_{coh}.

The melting temperature of the oxide is usually considered as a simple function of the bond energy. The relation between the melting temperature and the effective cohesive enthalpy (ΔH^{o}_{coh}) is plotted in **Fig.4**. The correlation is rather weak and the range where the points for different oxides are located is rather wide. The points for the oxides of metals from 12 group decidedly stand out, even if the slope of the corresponding line is similar. Also the points for the TiO, VO and NbO oxides do not lay on the same line. It is difficult to explain quite big differences in the melting temperature between the FeO, CoO and NiO oxides, while they have similar cohesive enthalpies, or the opposite situation for the M_2O_3 oxides of f-electron metals, which have similar melting temperatures and big differences in the cohesive enthalpies. One of the reasons can be the fact that the cohesive enthalpy analyzed is calculated at 298 K, while the bond energy and the character of its temperature dependence vary for different oxides. Furthermore, in the melting temperature only the crystal lattice is destroyed but the interactions between ions remain strong. As can be seen in Fig. 3, the melting enthalpy is about 10% of the cohesive enthalpy, therefore in a melted oxide the forces of cohesion are still significant. The lack of correlation is resulting also from the fact that the cohesive enthalpies of oxides describe the total bond energy in different volume elements.

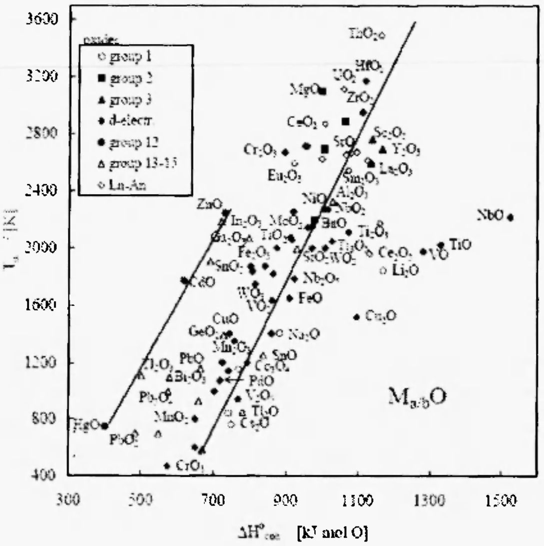

Fig. 4: The relation between the melting temperature of oxides and their effective cohesive enthalpy.

In the physico-chemical model the cohesive energy is defined as the energy needed to break a crystal, thus similarly as the surface tension it applies to one unit of surface resulting from the breaking of a column of the crystal. On the other hand, during atomization of one mole of crystal a break of a definite number of bonds occurs in the M_aO_b oxide (i.e. bonds between *a* moles of metal atoms and *b* moles of oxygen atoms, which together form a definite molar volume, $V_{M_aO_b}$). An intensive parameter, that characterizes the bond energy of a crystal, can thus be the ratio of the molar cohesive enthalpy to the molar volume, which would describe the bond energy in a volume unit. This parameter will be further called the *density of molar cohesive enthalpy* ($\Delta H^{\rho}_{\mathrm{coh}\ M_aO_b}$):

$$\Delta H^{\rho}_{\mathrm{coh}\ M_aO_b} = \Delta H^{M}_{\mathrm{coh}\ M_aO_b} / V^{M}_{M_aO_b} \qquad (10)$$

As the molar volume can be calculated basing on known lattice parameters or X-ray density (ρ_X):

$$\rho_X = Z M_{M_aO_b} 1.6604/V_{M_aO_b} \qquad (11)$$

where Z stands for the number of M_aO_b molecules of molar mass $M_{M_aO_b}$ which are contained in an unit cell of volume $V_{M_aO_b}$. Thus the density of the molar cohesive enthalpy can be calculated using the formula:

$$\Delta H^{\rho}_{\mathrm{coh}\ M_aO_b} = \Delta H^{M}_{\mathrm{coh}\ M_aO_b} \rho_X / Z M_{M_aO_b} 1.6604 \qquad (12)$$

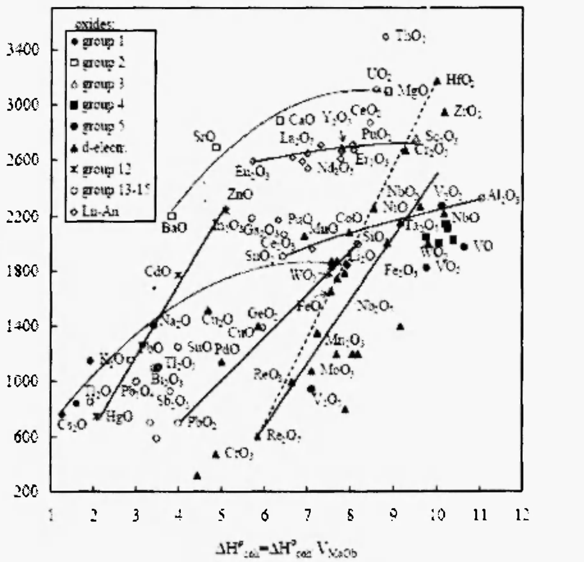

Fig. 5: The relation between the melting temperature of oxides and the density of the molar cohesive enthalpy.

In the case of lack of crystallographic data the experimental density can be used for the calculation of the density of the cohesive enthalpy. The experimental density is usually lower because of errors resulting from polycrystallity of the material (grain boundaries, defects etc.). Also the density of a monocrystal will differ from the X-ray density because of the concentration of defects. In the case of non-stoichiometric compounds or ordered structures, the differences between the experimental density and the X-ray density can be related to the difficulties in the composition determination, (determination of the real number of molecules in the unit cell). In **Fig. 5** the melting temperature of many oxides is plotted against their densities of the cohesive enthalpy. Generally, there is no correlation between the studied parameters. Nevertheless, some oxides with similar properties or similar bond character show quite good correlations. The MO_2 oxides of the actinides (ThO_2 and UO_2) and the oxides of alkaline earth metals have the highest melting temperatures. The M_2O_3 oxides of the lantanides and the oxides of 3rd group metals have lower melting temperatures but the dependence of T on $\Delta H^{p}_{\mathrm{coh}\ M_aO_b}$ has a similar nature. The HfO_2, ZrO_2 and Cr_2O_3 oxides should be included in the group of high-melting oxides. The next group of oxides with lower melting temperature and similar character of the dependence is formed by Ga_2O_3, MnO, CoO, NiO and Ta_2O_5, NbO_2, NbO, V_2O_3 Ti_2O_3, Al_2O_3. The melting temperature of the M_2O oxides of alkali metals increases monotonically with the increase of $\Delta H^{p}_{\mathrm{coh}\ M_aO_b}$. However, the practically linear character of the dependence of T on $\Delta H^{p}_{\mathrm{coh}\ M_aO_b}$ is observed in the oxides of 3d metals (NiO, CoO, Fe and Mn oxides (without MnO)). The points for the Cr_2O_3, ZrO_2, HfO_2 oxides lay close to the above line. A linear relation is observed also for the oxides with ions in higher oxidation state (WO_3, Nb_2O_5, ReO_3 Re_2O_5). The line for oxides with ions in higher oxidation state: NbO_2, Ta_2O_5, MoO_2, MoO_3, ReO_3, Re_2O_7 and V_2O_5 has a similar slope. Attention should be paid to the narrow range of the energies of cohesion and similar melting temperatures of Ti and V oxides and NbO, as opposed to the relation shown in Fig. 4. A very good linear correlation of similar slope is observed for ZnO, CdO and HgO, although also the correlation for ZnO, CdO and In_2O_3 could be analyzed. As can be seen in Fig. 5, the density of the molar cohesive enthalpy for respective groups of oxides is in good correlation with their melting temperatures, while both melting temperature and character of relation depend obviously on the bond character. The present analysis implies that the melting temperature of the oxides is not a simple function of the cohesive enthalpy or the density of the cohesive enthalpy, while the $\Delta H^{p}_{\mathrm{coh}\ M_aO_b}$ parameter allows correct conclusions to be drawn for individual groups of oxides with similar properties.

6. CONCLUSION

The present analysis of the effective cohesive enthalpy of oxides depending on their composition allows the formulation of the following conclusions:

1. Using the enthalpy of formation of M_aO_b oxides along with the enthalpy of metal sublimation and the enthalpy of oxygen dissociation, one can calculate the effective enthalpies of cohesion of $M_{a/b}O$ oxide (Eq. 3) which describe the total energy of the interaction of a/b moles of metal with one mole of oxygen. This parameter allows the comparison of the oxides of various compositions.
2. The cohesive enthalpy (per one mole of oxygen atoms) of the oxides of the same metal decreases with the content of metal and this relation is linear, even if in the individual oxides the ions of metal are in different oxidation states, and in the oxides with mixed valence and non-stoichiometric phases the ratio of metal ions with different charges is variable.
3. The linear relations obtained for the composition dependence of $\Delta H^{o}_{\mathrm{coh}}$ allow calculation of the cohesive enthalpy of the oxide phases of the same metal if their composition is known.
4. The slope of the lines obtained is dependent on the ionic-covalent character of bond (the electrostatic interaction). The steepest composition dependence of the cohesive enthalpy is observed for the oxides of d-electron metals: Nb, Ti, V, Cr, Re, Os, Ru, Mo,

W and f-electron metals: U, Tb, Pr Ce, lower slope can be seen for the oxides of Mn, Fe, Co and Pu, Am, the smallest slope is observed for the Cu, Ag oxides and the oxides of main groups metals: Pb, Sn, Tl.

5. The lack of the MO or M_2O_3 oxides of high-melting metals in the crystalline state results from the fact that these oxides do not reach the cohesion enthalpy high enough to satisfy the condition of their stability (8). This is due to the increase of the repulsive contribution to the interaction of the M^{3+} or/and M^{2+} ions, when the content of metal ions in the oxide increases (M/O ratio increases), and also by too high enthalpy of sublimation of these metals.
6. It has been proved that there is a correlation between the melting enthalpy of the oxides and their melting temperature.
7. The melting temperature of the oxides is not a simple function of the cohesive enthalpy and is dependent on the type of metal and the character of bond.
8. The proposed parameter: the density of the cohesive enthalpy allows to determine the dependence of the melting temperature on this parameter for the respective groups of oxides with similar character of bond.

REFERENCES

1. J.A Duffy, *Bonding, Energy Levels and Bands in Inorganic Solids*, Longmans, New York, 1990.
2. N. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford Univ. Press, London, 1954.
3. W.A. Harrison, *Electronic Structure and the Properties of Solids*, Freeman, San Francisco, 1980.
4. R.G. Pearson, *Chemical Hardness*, J. Wiley-VCH, New York, 1997.
5. C. Kittel, *Introduction to Solid State Physics*, J. Wiley, New York 1997.
6. R.W. Grimes, C.R.A. Catlow and A.L. Shluger (editors), *Quantum Mechanical Calculations in Solid-State Studies*, World Scientific, Singapore, (1992).
7. C.R.A. Catlow, *Computer Modeling in Inorganic Crystallography*, Academic Press. London, 1997.
8. A. Stoklosa and B. Wzorek, *High Temp. Mater. Proc.*, **23,** 103, (2004).
9. D.R. Lide (editor), *CRC Handbook of Chemistry and Physics,* CRC Press, Boca Raton, 2004.
10. O. Kubaschewski and C.A. Alcock, *Metallurgical Thermochemistry*, Pergamon Press. Oxford, 1979.
11. L.B. Pankratz, *Thermodynamic Properties of Elements and Oxides, Bulletin* 672, U. S Bureau of Mines, Washington, 1982.
12. *Thermochemical Properties of Inorganic Substances*, J. Barin O. Knacke (eds), Springer-Verlag, Berlin, New York, (1973), Supplement (1997); O. Knacke, O. Kubaschewski and K. Hasselmann (editors), 1991.
13. E.H.P. Cordfunke and R.J.M. Konings, *Thermochemical Data for Reactor Materials and Fission Products*, North-Holland, Amsterdam, 1990.